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Interconnected mesoporous Na_2FeSiO_4 nanospheres supported on carbon nanotubes as a highly stable and efficient cathode material for sodium-ion battery

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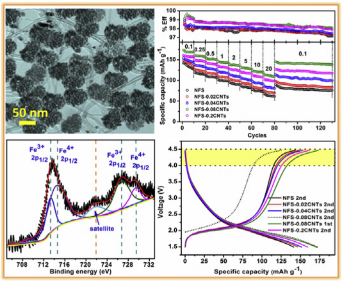
HIGHLIGHTS

- Mesoporous Na_2FeSiO_4/CNTs composite is prepared via a modified two-step route.
- Presenting the possibility of more than one sodium extraction between 1.5 and 4.5 V.
- Composite delivered impressive sodium storage performance of 172.9 $mAhg^{-1}$ at 0.1C.
- The discharge capacity is remarkable even at the high current rate of 20C.
- The amount of CNTs added greatly influence electrochemical performance of Na_2FeSiO_4.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured sodium metal orthosilicates hold a lot of promise as next-generation cathodes but their practical application is hindered by the complex crystal structure and electrochemical behaviour. Herein, cubic polymorphs of Na_2FeSiO_4 with F-43 m symmetry decorated on carbon nanotubes have been synthesised successfully using a novel two-step process. The composite material with 0.08 wt% of carbon nanotubes demonstrate a capacity corresponding to a 1.25 sodium-ion exchange process resulting in 172.9 mAh g^{-1} at 0.1C cycled in the voltage range between 1.5 and 4.5 V. This work also highlights the mechanism of insertion/extraction process using complementary techniques of X-ray photoelectron spectroscopy, and X-ray diffraction revealing the involvement of Fe 3 d band and conversion of Fe^{+2} to Fe^{+3} during first sodium-ion extraction while second sodium-ion extraction is possible due to further oxidation of Fe^{+3}. The discharge capacity is remarkable even at the high current rate of 20C, where we obtained the final capacity of 109.3 mAh g^{-1}. The excellent electrochemical performance reported here is due to the high structural stability of Na_2FeSiO_4 composed of rigid corner-sharing tetrahedra, improved electronic conductivity by carbon nanotubes, reduced particle size, increased defect structure, high sodium-ion diffusion coefficient and the decreased charge transfer resistances.

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1. Introduction

Batteries are considered to be most vital for emerging green technologies providing mobile energy storage with high energy densities. In particular, lithium-ion batteries (LIBs) dominate today's market due to small size ($Li^+ = 0.76$ Å) for easy insertion reaction, low redox potential and light in weight (6.9 g mol^{-1}). Efforts have been focused on other battery systems like lithium-O_2 and lithium sulphur but the adaptation of these technologies faces serious concerns due to high cost and limited natural abundance of lithium. Increased demand for mid to large scale batteries for electric vehicles and energy storage systems (ESS) may result in serious problems such as shortage of lithium resources in the near future. Sodium-ion batteries (SIBs) are considered as a desirable substitute for LIBs due to high natural availability and consequently the low price of sodium [1]. However, the potential battery performance is low for SIBs in comparison to LIBs due to 55% larger size ($Na^+ = 1.02$ Å) and more than three times heavier in weight (23 g mol^{-1}) which limits the intercalation rate and associated diffusion processes. Even so, the low cost of sodium can provide sufficient advantage for adaptation as compared to lithium, therefore research on SIBs is drawing ever more scientific enthusiasm and a strong progress made in LIBs is likely to be repeated in SIBs [2,3].

Another obstacle in the mass production of batteries is the high cost of most usual raw materials (Ni and Co) associated with current battery technologies. Therefore, the SIBs that use inexpensive sodium based metal oxides (Fe and Si) as cathodes are potential alternatives. The Na-Fe-Si-O system of the silicate family having strong $Si-O$ bonds and cheapest raw materials offer great promise as it is anticipated to have the same lattice stabilization effect as in $LiFePO_4$ [4]. Lithium-based silicates (Li_2MSiO_4; M = Fe, Mn, Co) have been previously investigated with successful capacity outcomes due to the possibility of two electron exchange process [5–11]. However, there are limited reports on sodium based silicate analogues (Na_2MSiO_4, M = Fe, Mn, Co) due to their major drawback of characteristically low electronic conductivity and obtaining a phase pure material [12–16]. The common solid-state synthesis methods always result in some impurities like Na_2SiO_3, Fe_3O_4, Fe_2SiO_4 etc, therefore in order to avoid any impurity phase various solution based synthesis techniques such as refluxing method and sol-gel assisted solvothermal methods have been practised to prepare nanoparticles of silicate family [16]. The first evaluation of electrochemical activity of sodium based silicates was conducted on Na_2MnSiO_4 with a specific capacity of 125 mAh g^{-1} at 0.1C rate using an ionic liquid electrolyte [13]. Later, Na_2FeSiO_4 (NFS) was synthesised and is reported to exhibit a specific capacity of 106 mAh g^{-1} [16] and carbon coated NFS with 181 mAh g^{-1} [17]. Na_2CoSiO_4 is found to yield specific capacity of 100 mAh g^{-1} at 5 mA g^{-1} [12]. Among these, NFS is most attractive as it can turn out to be the cheapest cathode material due to large resources of Na, Si, and Fe, however, it has low ionic and electronic conductivity.

Coating with carbon is one method to decrease the particle size and accelerate charge transfer but the usual coating methods of mixing NFS with carbon source and annealing at high temperature suffer from the unsatisfactory coating and expected crystal growth at higher temperatures, therefore up till now, only one such report can be seen where more than one sodium extraction has been observed in NFS [17]. Although carbon coating often results in an improved capacity for initial cycles however due to weak interactions with metal particles and poor electrolyte infiltration the long cycle lifespan and power density is strongly affected [18]. Carbon nanotubes (CNTs) with their tubular structure, superior conductivity, favourable surface area, high flexibility and chemical stability are particularly suited for wiring active material and numerous such reports on CNTs based nanocomposites for SIBs application can be found in the literature [19,20]. Compared to famous graphene sheets CNTs offer open channel structure and act as smart electronic wire and reliable support network for active materials during electrochemical cycling. Thus by strongly binding active materials on CNTs surface with interweaving network, the issues like the weak interaction of active material and carbon coating, slow sodium-ion diffusion and unstable solid electrolyte interface (SEI) can be addressed [21].

In this study, we explored the synthesis of phase pure NFS nanoparticles and its interaction with flexible CNTs for electrical wiring and interweaving these nanoparticles which contribute to more than one electron extraction from NFS and excellent rate capability for the composites. The mechanism point out that two-stage oxidation of primary Fe^{2+} results in an extra capacity beyond 4.0 V and the extraordinary stability imparted by Fe-Si framework together with CNTs keeps excellent reversibility during sodium extraction/insertion.

2. Experimental

2.1. Growth of CNTs

CNTs were prepared in form of vertical columns on a silicon wafer by simultaneously flowing carbon source and nanocatalyst using chemical vapour deposition (CVD) method. Ferrocene was used as a catalyst precursor for preparing iron nanoparticles while commercial camphor bearing pentagonal and hexagonal carbon rings was used as a carbon source. Briefly, a steel tube was positioned inside a three-zone tube furnace and the temperature was adjusted to 850 °C under an inert atmosphere. The central region of the steel tube was reserved for silicon substrates and nitrogen gas flux (420 ml min^{-1}) was used to maintain the inert atmosphere. Camphor and ferrocene (20:1) were mixed in a Pyrex conical flask which was then heated to 200 °C and the vapours so formed were transported to the silicon substrate under a continuous flow of nitrogen. The pyrolysis of vapours on the surface of silicon resulted in the formation of CNTs carpet, with iron nanoparticles acting as a catalyst. The reaction was stopped after 60–90 min after attaining the desired thickness of the CNTs carpet.

2.2. Purification and functionalization of CNTs

In order to eliminate the amorphous carbon present in raw CNTs, they were oxidised in air for 4 h at 450 °C in a furnace. The oxidised CNTs were then suspended in 3 M HCl and refluxed for 30 min to eliminate any trapped catalyst particles. The resulting black solution was centrifuged at ~6000 rpm and the transparent brownish yellow liquid is poured out. The black sediments sticking at the sides and bottom of the centrifuge tube still, contain considerable trapped acid which was removed by shaking the sediments vigorously with deionized water and repeating the centrifugation many times until the solution becomes neutral.

Purified CNTs were mixed with a mixture of 6 M $NaNO_2$ and 6 M HCl (1:1.5) and sonicated for 8 h in an ice bath. The paste so formed was filtered through membrane filter paper of 0.22 µm pore size after diluting it with deionized water and the solid collected was rinsed many times with deionized water unless the filtrate becomes neutral. The as-obtained functionalized CNTs were dried at 120 °C for 1 h.

2.3. Synthesis of sodium iron silicate (NFS)/CNTs composite

The composites were synthesised by using reflux assisted sol-gel method. Typically, 0.1 M PVP solution was prepared in ethanol followed by addition of 5 ml ethylene glycol (EG) under stirring until a transparent uniform solution was obtained at room temperature. Functionalized CNTs with different wt% were added into the transparent solution to obtain samples with varying CNTs concentration (x = 0.00, 0.02, 0.04, 0.08, 0.2). After sonicating the above solution for 1 h the stoichiometric amounts of sodium acetate ($NaCH_3COO·2H_2O$) and iron(II)oxalate ($FeC_2O_4.H_2O$) were then added to the stirring solution at 45 °C under an inert atmosphere. After 1 h of continuous stirring, tetraethyl orthosilicate (TEOS) was dropwise added and the